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Lecture – 49 Retention of Pollutants on and Within Soil Solid Phases (Contd.,)

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Welcome friends to this fourth lecture of this online certification course of environmental soil chemistry and in this week we are basically talking about the retention of pollutants on to the soil solid phase.

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So in our previous lecture we ended here we started talking about the kinetics of adsorption and I told you that the characteristics, the period of ion exchange in soil basically ranges from few seconds to days and basically this is due to the properties of inorganic and organic constituents of the soil solid phase and also the properties of the pollutants ion charge as well as their radius.

The slowly exchangeable cations are basically situated in the exchange sites in interlayer space of the soil minerals like mica or in cages of channels of soil organic matter and exchange out into the solution by diffusive flux we already know that. So what are the other important aspects of this kinetics of adsorption so also we see that ion exchange occurs when a driving force. So ion exchange basically occurs through a driving force where basically the driving force is either a chemical potential gradient.

A chemical potential gradient which is maintained between solid and solution or when the access to the site is freely maintained by; the use of a hydrated and less preferred cations for exchange. So, these two are the driving force for solution. First of all, the chemical potential gradient which is maintained between the solid and solution that is one of the driving force of ion exchange.

Another is when the access of the site is freely maintained for the adsorption by the use of hydrated and less preferred cation for exchange. So when there is a hydrated and less preferred cation for exchange. Obviously the pollutants can exchange those hydrated and less preferred cations and then get adsorbed. So there is a competition and these pollutants basically wins this competition to get adsorbed into the clay surface.

So as we previously shown in the case of most organic non ionic compounds of interest like organic pollutants and pesticidal chemicals that is environmental contaminants. The driving force for adsorption consists of entropy changes and relatively weak enthalpic forces. So, we have already discussed those entropic based and enthalpy based forces. Now remember that hydrophobic bonding to the soil organic phase may be the most important interaction for neutral molecules we have already discussed this hydrophobic bonding.

Remember that hydrophobic moiety getting attached to the clay surface or organic matter we have discussed in detail. So, these processes basically defines the kinetics of adsorption of these organic pollutant which are specifically hydrophobic in nature.

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Now if we move ahead and see the sorption of these molecules by soils are generally been characterized by an initial rapid rate followed by a much slower approach to an apparent equilibrium. So basically the adsorptions of these chemicals basically are very fast in the initial phase to a much and then they become slower as the time progresses and then they reaches an apparent equilibrium.

Now the; initial reactions have been associated with the diffusion of the organic toxic compounds. So the initial reaction have been associated with the diffusion of the organic toxic compounds to and from the surface of the sorbent. So, either to the surface of the sorbent in our case this is soil or from the surface of the sorbent these movement or diffusion of the organic toxic compounds are responsible for the initial high rate.

Now while the slower reactions have been related to the particle diffusion control of the movement of the molecules in and out of the micro pores of the sorbent. So when the movement of the molecules in and out of the micro pores of the sorbent are basically concerned then it is showing the slower rate. So initially it is high fast rate and then it is becoming slower and then it becomes equilibrium.

Now diffusion will be seen to be an important factor determining the release of the pollutant obviously from this discussion it is very clear the diffusion is the one of the major processes for desorption of the organic pollutants from the soil solid phase.

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Now what are the factors affecting the adsorption? Obviously there are numerous factors which basically controls the adsorption of these organic and inorganic pollutants. Now the mechanism, extent and rate of adsorption process are basically controlled by environmental factors. What are those three environmental factors? First of all, soil constituents then soil moisture content and then temperature. So these are the major three controlling factor.

Now remember that the mineralogical composition of the soil is one of the major factors in defining the rate and extent of the ion exchange and this is related to the structural properties of the clay mineral. We have already known that the structure of the clay mineral varies from one another and due to the variation in the structure obviously the mineralogical composition also differ and as a result of the change in the mineralogical composition and their structure their adsorption characteristics also differs from each other. Let us see some examples although we have discussed them, but let us see some specific examples.

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So if we consider the clay mineralogy now in the case of Kaolinite, the tetrahedral layers the adjacent clay sheets are tightly held together by hydrogen bonds and only planer external surface sites are available to exchange. So what you can see here this is Kaolinite structure and the inter particle sites are basically there is almost nil internal distance. So, basically due to the presence of hydrogen bonding.

As a result of that, the only planar external surfaces sites are available for exchange. So here these planar external sites are available for different types of exchange of different pollutants. So this is, so you can see here the structure or specific structure of the clay mineralogy is affecting the, affecting or controlling the sites where these exchange reactions for adsorption are occurring.

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Now in case of smectite, in case of smectite, what do you see? Specifically in case of montmorillonite which is one of the most important and expanding clay mineral. We can see that clay particles are able to swell obviously if there is an adequate hydration followed for a rapid passage of ions to the interlayer space. We have also discussed here so here there are two layers so this is an interlayer space.

In the interlayer space this is, you know, the interlayer space is quite high so variable spacing you can see and also in this huge interlayer space you can see the hydrated exchangeable cations are there, okay. So due to the presence of this hydrogen exchange in cations also these interlayer space is one of the major controlling factor of the adsorption of pollutants, okay.

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Now in case of vermiculite obviously if you remember the structure of the vermiculite which are shown here these vermiculite minerals is characterized by more restructured interlayer space since the region between the layers of the silicate is selective for certain types of cations such as potassium and ammonium. So this is also region between the interlayer is basically can be occupied by certain elements, certain cations like potassium like magnesium like ammonium.

So you can see one thing that clay mineralogy takes an important part in the determining the rate and the species of the pollutants which are getting adsorbed in different sites. In case of Kaolinite, it is totally external site however in case of, you know, vermiculite, and in case of montmorillonite their sites are more or less internal in nature. So obviously due to the

presence of this interlayer and external layer adsorption obviously the reaction rates also varies from one clay mineral to another clay mineral, okay.

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So we have seen that the main properties affecting the adsorptive capacity of the clays are considered to be basically three. First of all, the available this is basically the available surface area and the cation exchange capacity as well as the saturating cation. Secondly the hydration status it is one of the another important part and third one the surface acidity which is related to the two preceding properties of the clay structure.

So these two properties of the clay structure basically defines whether the, what is the nature of the surface acidity of the clay mineral, okay. So, it is basically due to the hydration status and also availability of the external surface area and the cation exchange capacity. So, these three are the major properties which are governing the adsorptive capacity of the clays.

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So if we move ahead and another important factor is soil pH. Now carboxyl and phenolic hydroxyl functional groups contribute most to the cation exchange capacity of the humus. Now you know that in case of humus we have already discussed carboxyl and phenolic hydroxyl functional groups are present and they contribute most to the cation exchange capacity of the humus.

Now for example uranic acid in polysaccharides and the acidic amino acid for example aspartic and glutamic acid and carboxy-terminal structures in peptides can contribute to the negative charge of the CEC, negative charge and CEC of the organic matter under appropriate pH conditions. So; negative charge and CEC of the organic matter can be contributed by uranic acid in polysaccharides and the acidic amino group for example aspartic acid and glutamic acid and carboxy-terminal structure in peptides. So as a whole they show a huge amount of negative charge and consequently cation exchange capacity.

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Now another important factor is the hysteresis factor. Now let us first define what is hysteresis considering the water, considering the soil water or content of the soil water. Now this graph basically shows the soil water retention curve. So hysteresis, what is hysteresis? Hysteresis in soil is basically defined as the difference in the relationship between the water content of the soil and the corresponding water potential obtained under wetting and drying process.

So basically we have seen that if we put the suction in the x axis and degree of saturation in the y axis and there are two curves we can see. One is for wetting during the wetting we will see one curve and during the drying we will see another curve, obviously during the drying the degree of saturation will move from 100 to eventually very low and also in the reverse process when we are wetting the soil.

We are getting continuously increase degree of saturation by reducing the suction. So, by reducing the suction we are getting continuously higher degree of saturation. Now one thing is clear at any point of suction the amount of the water content which is defined in terms of degree of saturation is always higher in case of dry curve than that of wetting curve. So this difference is, this phenomena is known as the soil hysteresis.

So, hysteresis in soil as the difference in the relationship between the water content so basically at this particular for example let us consider this particular suction. So at this air entry suction, let us consider this air entry suction so at this air entry suction you can see the degree of saturation in the wetting curve is far less than the degree of saturation in the main drying curve.

So this is called the hysteresis effect. So, hysteresis in soil is defined as the differences in the relationship between the water content of the soil and the corresponding water potential obtained under wetting and drying processes. So, the relationship between soil water content and the soil water potential so soil water potential has the same value as the soil water suction is known as the soil water retention curve so this is basically soil water retention curve. So this hysteresis properties of the soil also influencing the adsorption also can influence the adsorption.

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So hysteresis in desorption was observed for the humic acid and the mixture, but not for the clays. So this is how hysteresis affects the adsorption. So hysteresis in desorption was observed in case of humic acid and the mixture however in case of clay we could not find it. So hysteresis effect also we can see in case of organic matter. Now it should be pointed out that the organic material and mineral colloids relationship.

So there is a relationship between the organic material and mineral colloids rather than the isolated parameters must be considered in the assessment of the adsorption of organic pollutants by the soil. So that says that we should not consider organic matter and mineral colloids separate entity when we are talking about the adsorption of pollutants. We should consider the organic material and mineral colloid relationship as a whole while defining the adsorption kinetics in the soil solid phase.

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So, if we see the properties of organic matter. The properties of organic matter plays a very important role in the adsorption process in the soil solid phase. Now although the importance of organic matter in organic pollutants adsorption has been well established. The properties of the organic colloids which are relevant to adsorption have not been thoroughly characterized here. So there is need for more research in that area.

Now the available information shows that these properties could be the properties of the humic acid, fulvic acid and humin. The presence of the active groups such as carboxyl, hydroxyl, carbonyl, methoxy and amino group and also high cation exchange capacity of the surface area okay. So the; adsorption of the pollutants in the organic matter are basically governed by these factors.

The properties of the humic acid, fulvic acid and humin and the presence of the active group such as carboxyl, hydroxyl, carbonyl, methoxy and amino groups and also high cation exchange capacity and surface area. All these properties of organic matter plays a very important role while defining the adsorption. As you can see these are the important groups carboxyl group, phenolic group, alcoholic groups. All these groups play an important role you know while defining the adsorption by the soil organic matter.

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Factors affecting adsorption

- Soil environment
- In addition to the properties of soil components, the soil environment influences the distribution of synthetic organic chemicals among the soil phases.
- The environment of a specific soil is determined not only by its intrinsic properties, but also by external factors, especially climatic conditions and agricultural practices.
- · These factors affect the extent and timing of changes in the soil environment.



So let us move ahead and see the other important factors. Now among the other important factors soil environment. Now in addition to the properties of the soil component, the soil environment influences the distribution of synthetic organic chemicals among the soil phases and the environment of a specific soil is determined not only by its intrinsic properties, but also by external factors especially climatic condition and agricultural practices and these factors affect the extent and timing of changes in the soil environment.

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The next important factor is soil moisture. Now pesticides are usually transported to the adsorbing surface by water and the moisture content determine the accessibility of the adsorption sites and water affects the surface properties of the adsorbent. Now remember that the toxicity and chemical analysis of certain pesticide like DDT then gamma-BHC or

benzene hexachloride and dieldrin applied on the mud block showed that bioactivity closely followed any changes in humidity.

And that the rate of diffusion of the insecticide in the mud blocks increase with humidity. So if there is an increase in humidity the rate of diffusion of insecticides these specific insecticides like DDT, gamma BHC and dieldrin increases with increase in humidity through the mud block. So an experiment has already supported this. So soil moisture plays an important role for movement of these, you know, toxic pesticides.

And that the insecticide sorbed were reactivated by increased moisture content. So they have also seen that it can be increased the insecticides sorbed were reactivated by increasing the moisture content and the explanation for these behavior that there is competition for adsorption site between the water and this nonionic pesticide. So this is the reason that soil moisture plays an important role for adsorption of different organic and inorganic pollutants.

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The next important factor is pesticide clay water system. So, although the hydration of the clay and properties of adsorbed water are not fully yet understood I have already told you. So it is generally accepted that water molecules are attracted by the clay surface. So clay surface has a general affinity to the water molecules mainly by the exchangeable cations and form hydrations shells.

So exchangeable cation generally attract those water molecule and make the hydration shells then adsorbed water provides the adsorption site for pesticide molecules. So these adsorbed water provide adsorption sites for pesticides molecules. Now an important feature of water associated with clay surface is its increased dissociation giving the surfaces slightly acidic character.

So when it is dissociated, the clay surface is dissociated it increased the dissociation so it basically shows the acidic characteristics. pH dependent charge is mostly dependent on these type of dissociation and as a result of that when the pH changes, the external surface of the broken edges the hydroxyl groups in the broken edges get different positive or negative charges and as a result they basically attract different types of organic and inorganic pollutants species.

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Factors affecting adsorption Effect of hydration of SOM: It has been suggested that hydration influences the molecular shape of humic substances, and thus accessibility for pesticides. Strong, sometimes irreversible, retention of pesticides by hydrated humic substances could be explained by the penetration and trapping of pesticides into the Internal structure of the swollen humic substances. At low moisture contents, the hydrophobic portions of the organic matter structures could bind hydrophobic, nonionic pesticides.

Now effect of hydration of soil organic matter. It has been suggested that hydration influences the molecular shape of humic substances and thus the accessibility of the pesticide. Now remember that strong sometimes irreversible retention of pesticide by hydrated humic substance could be explained by the penetration and trapping of the pesticides into the internal structure of the swollen humic substances.

So sometimes these toxic humic substance penetrate into the structure of the organic matter and get their trapped and as a result of that these, you know, the process is irreversible they cannot come out. At low moisture content the hydrophobic portion of the organic matter structures could bind hydrophobic nonionic pesticides you have already seen this before. (Refer Slide Time: 22:29)

Factors affecting adsorption

Soil temperature

Sway

- As the adsorption processes are exothermic, changes in soil temperature could have a direct effect on the phase distribution of pesticides.
- Adsorption usually increases as the temperature decreases, and desorption is favored by increasing temperature.
- Temperature could indirectly influence adsorption by its effect on pesticide-water interactions.

The next important factor is soil temperature. Now remember as the adsorption process are exothermic, that is temperature producing. When some reaction occurs, so if that reaction generates some heat that is exothermic reaction. Now as the adsorption processes are exothermic in nature changes in soil temperature could have a direct effect on the phase distribution of the pesticide.

Now adsorption usually increases as the temperature decreases and desorption is favored by increasing temperature. The temperature could indirectly influence adsorption by its effect on pesticide water interaction.

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Now the adsorption temperature relationship reflects not only the influence of energy on the adsorption process, but also the change in solubility of the adsorbate because solubility is a

property which changes drastically with the temperature driven, but the change in activity in solution are important as the difference between the activity in solution and the adsorbent is the driving force in the adsorption process. So temperature plays an important role in the adsorption of organic or inorganic pollutants into the solid solids.

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Now let us talk about another important thing that is called non-adsorptive retention. Now in the non-adsorptive retention it basically shows the processes these processes so non-adsorptive retention of the process which have been somewhat neglected until now. So far we focused only on adsorptive retention processes. So non adsorptive retention processes are neglected until now.

Despite the fact that they provide important mechanism for pollutant retention in the soil medium. Now it basically depends on two important processes one is called pollutant precipitation and the second one is called the trapping so we will discuss both of them.

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Non-adsorptive retention

- Pollutant Precipitation:
- If adsorption was defined as a net accumulation at an interface, precipitation can be defined as an accumulation of a substance to form a new bulk solid phase.
- Sposito (1984), defining this process, showed that both of these concepts imply a loss of material from an aqueous solution phase, but one of them is inherently two-dimensional and the other inherently three-dimensional.



So we will start first with the pollutant precipitation. So pollutant precipitation if adsorption was defined as a net accumulation at an interface, precipitation can be defined as an accumulation of a substance to form a new bulk solid phase. So this is the difference. The adsorption is basically a net accumulation at an interface. However, precipitation can be defined as an accumulation of a substance to form a new bulk solid phase.

So in case of precipitation there is a formation of new bulk solid phase. Now, Sposito in 1984 defined the process showed that both these concepts imply a loss of material from an aqueous solution. So basically this precipitation or adsorption both of them are occurring from the cations or anions which are basically present in the solution. So both of these concepts imply a loss of material from the aqueous solution phase.

But one of them is inherently two dimensional so obviously the adsorption is two dimensional and the other are inherently three dimensional. So if we consider the pollutant precipitation so if adsorption was defined as a net accumulation at an interface, precipitation can be defined as an accumulation of a substance to form a new bulk solid phase. So obviously you can see that, you know, in case of adsorption it is only an accumulation at an interface.

However, in case of precipitation it occurs as a formation of a new bulk solid phase. Now the scientist Sposito has defined this process and shown that both of these concepts imply a loss of material from an aqueous solution phase because all these ions are basically present in

aqueous solution phase and from there they get either adsorbed or they get precipitate in a new bulk solid phase.

However, these adsorption process is two dimensional and the precipitation process is inherently three dimensional in nature because it is forming a new bulk solid phase. So this is the difference between these two.

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 The precipitation is never complete and the precipitates have their own solubility products, and 	Heavy metal	pKa
liquid.	Cd ²⁺	8.7
Heavy and transition metals are present a	• Co ²⁺	8.9
hydrated cations in water at neutral pH values an	d Cr ²⁺	6.5
at this stage they behave like acids, due to wate	r Cu ²⁺	6.7
molecule dissociation in the hydration shell of th	e Mn ²⁺	10.6
cation.	Ni ²⁺	8.9
• The "acidity" of hydrated cations depends on th	e Pb ²⁺	7.3
pK _s , values of which are presented in Table.	Zn ²⁺	7.6
 From the data presented in Table, it can be deduce 	Fe ³⁺	3.0 -
that the lower the pK _s value of the metal the lower	r	V
will be the pH at which precipitation takes place.	pK, values of the major h	ieavy metal

Now so the precipitation is never complete obviously the precipitation is never complete and the precipitation have their own solubility products obviously and thus ions are always present in supernatant liquid. So precipitation cannot be completed it always goes on and the precipitation have their own solubility products and thus the ions are always present in the supernatant liquid which is present.

Now heavy and transition metals are present as hydrated ions in water at neutral pH values and at this stage, they behave like acid due to the water molecule dissociation in the hydration shell of the cation. So basically these neutral and these heavy, sorry, these heavy and transition metals are present as hydrated cations and due to the dissociation of the hydration shells of this cations, they behave as a, behave like acids.

Now the acidity of hydrated cation depends on the pKa values which is presented in this table you can see now we have already defined the pKa values it is a negative logarithm of Ka values. So lower the pKa values means higher the acidity so we can see from the data from this table that the lower the pKa value of the metal, the lower will be pH. So here you can see the Fe3 + has the lowest pKa value among all these.

So the lower the pKa value of the metal, the lower will be the pH at which precipitation takes place. So, obviously their precipitation will take place at lower pH since they have lower pKa value that means they are more acidic in nature. So this is an example of non adsorptive retention. So let us wrap up our lecture here in the last lecture that means it is the fifth lecture, we will be talking more about some of the examples of organic and inorganic pollutants adsorption and also we will be talking about the trapping of pollutants in details.

So let us wrap up this lecture here. If you find any difficultly just let me know, send me an email and I will be more than happy to answer your queries. Thank you very much let us meet in our last and next lecture. Thank you.